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(54) Title: HYDROCARBON HYDROGENATION CATALYST AND PROCESS

(57) Abstract: A catalyst composition which can be used for hydrogenating a highly unsaturated hydrocarbon such as an alkyne or a diolefin to a less unsaturated hydrocarbon is disclosed. The catalyst composition contains palladium, an inorganic support, and a catalyst component of silver and an alkali metal compound. The catalyst composition can additionally contain a halide, preferably a halide of a non-alkali metal halide. A process of making such catalyst composition is also disclosed. The process of using such catalyst composition involves contacting a hydrocarbon-containing fluid, which contains a highly unsaturated hydrocarbon, with a catalyst composition in the presence of hydrogen under a hydrogenation condition sufficient to effect a hydrogenation of the highly unsaturated hydrocarbon. The process of using such catalyst composition can be conducted in the presence or absence of a sulfur impurity such as a sulfur compound.

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HYDROCARBON HYDROGENATION CATALYST AND PROCESS  
BACKGROUND OF THE INVENTION

This invention relates to a catalyst composition and to a process of using such catalyst composition for hydrogenating a highly unsaturated hydrocarbon.

5           It is known to one skilled in the art that a less unsaturated hydrocarbon compound can be produced by a thermal cracking process. For example, a fluid stream containing a saturated hydrocarbon such as, for example, ethane, propane, butane, pentane, naphtha, and the like and combinations thereof can be fed into a thermal (or pyrolytic) cracking furnace and within the furnace the saturated  
10   hydrocarbon is converted to a less unsaturated hydrocarbon compound such as, for example, ethylene or propylene. Such less unsaturated hydrocarbons are an important class of chemicals that find a variety of industrial uses. For example, ethylene can be used as a monomer or comonomer for producing a polyolefin. Other uses of less unsaturated hydrocarbons are well known to one skilled in the art.

15           However, such less unsaturated hydrocarbon(s) produced by a thermal cracking process generally contains an appreciable amount of undesirable highly unsaturated hydrocarbon(s) such as alkyne(s) or diolefin(s). For example, ethylene is generally contaminated with a highly unsaturated hydrocarbon, such as acetylene, which must be selectively hydrogenated to a less unsaturated hydrocarbon, such as  
20   ethylene, but not to a saturated hydrocarbon such as ethane in a hydrogenation process. Similarly, propylene is generally contaminated with acetylene, methylacetylene, and propadiene which must be selectively hydrogenated to a less unsaturated hydrocarbon, such as ethylene or propylene, but not to a saturated hydrocarbon such as ethane or propane in a hydrogenation process.

25           In addition, catalysts comprising palladium and an inorganic support, such as alumina, are known catalysts for the hydrogenation of highly unsaturated hydrocarbons such as alkynes and/or diolefins. In the case of the selective hydrogenation of acetylene to ethylene, a palladium and silver catalyst supported on an alumina can be employed. See for example U.S. Patent No. 4,404,124 and  
30   divisional U.S. Patent No. 4,484,015, the disclosures of which are incorporated herein by reference. The operating temperature for this hydrogenation process is selected such that essentially all highly unsaturated hydrocarbon such as alkyne

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(e.g., acetylene) is hydrogenated to its corresponding less unsaturated hydrocarbon such as alkene (e.g., ethylene) thereby removing the alkyne from the product stream while only an insignificant amount of alkene is hydrogenated to a saturated hydrocarbon such as alkane (e.g., ethane). Such a selective hydrogenation process  
5 minimizes the loss of desired less unsaturated hydrocarbons and, in the front-end and total cracked gas processes, avoids a "runaway" reaction which is difficult to control.

It is also generally known to those skilled in the art that impurities, such as carbon monoxide, and sulfur impurities, such  $H_2S$ , COS, mercaptans and  
10 organic sulfides, which can be present in an alkyne-containing feed or product stream can poison and deactivate a palladium-containing catalyst. For example, carbon monoxide is known to temporarily poison or deactivate such hydrogenation catalyst. It is also generally known by those skilled in the art that a sulfur impurity  
15 such as a sulfur compound (such as  $H_2S$ , COS, mercaptans, and organic sulfides) can poison and deactivate hydrogenation catalysts. Since many plants run with various sulfur impurities continuously present or at least present as intermittent spikes, it would be advantageous to be able to run both in the presence of and  
20 absence of such various sulfur impurities. Sulfur impurities are usually found in depropanizer and raw gas hydrogenation processes (but can occur in any hydrogenation process) as a result of plant and operational limitations. The feed stream  
being sent to the acetylene removal unit (also referred to as "ARU") can contain either low levels and/or transient spikes of a sulfur impurity. Thus, the  
development of a catalyst composition and its use in processes for the hydrogenation  
of highly unsaturated hydrocarbons such as diolefins (alkadienes) or alkynes to less  
25 unsaturated hydrocarbons such as monoolefins (alkenes) both in the presence of and in the absence of a sulfur impurity, such as a sulfur compound, would be a significant contribution to the art and to the economy.

#### SUMMARY OF THE INVENTION

It is desirable to provide a catalyst composition that can be used for  
30 selectively hydrogenating a highly unsaturated hydrocarbon, such as an alkyne or diolefin, to a less unsaturated hydrocarbon(s) such as an alkene(s). Such catalyst composition can be useful as a catalyst in the hydrogenation of a highly unsaturated

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hydrocarbon to a less unsaturated hydrocarbon wherein a sulfur impurity such as a sulfur compound can be present.

Again it is desirable to provide a method of making such catalyst composition and to provide a process of using such catalyst composition to  
5 hydrogenate a highly unsaturated hydrocarbon, such as an alkyne or diolefin, to a less unsaturated hydrocarbon, such as an alkene, without further hydrogenation to a saturated hydrocarbon, such as an alkane.

An advantage of this invention is that there is a decreased selectivity to undesirable byproducts such as oligomers of acetylene as compared to a catalyst  
10 composition prepared by methods other than the inventive process(es) disclosed herein.

According to a first embodiment of this invention, a catalyst composition is provided which can be used for selectively hydrogenating a highly unsaturated hydrocarbon such as, for example, an alkyne or a diolefin, to a less  
15 unsaturated hydrocarbon such as an alkene. The catalyst composition comprises palladium, an inorganic support, and a catalyst component comprising silver and an alkali metal compound. The catalyst composition can further comprise a halide, preferably a halide of a non-alkali metal halide. Such catalyst composition can be prepared by a process comprising incorporating an inorganic support with palladium  
20 and a catalyst component comprising silver and an alkali metal compound. The catalyst composition can also be incorporated with a halide, preferably of a non-alkali metal halide.

According to a second embodiment of this invention, a process which can be used for selectively hydrogenating a highly unsaturated hydrocarbon to a less  
25 unsaturated hydrocarbon is provided. The process comprises contacting a hydrocarbon-containing fluid comprising a highly unsaturated hydrocarbon with a catalyst composition in the presence of hydrogen under a hydrogenation condition sufficient to effect a selective hydrogenation of the highly unsaturated hydrocarbon. Additionally, such hydrogenation process can be conducted in the presence or  
30 absence of a sulfur impurity such as a sulfur compound. The catalyst composition can be the same as the composition disclosed in the first embodiment of this invention.

Other objects and advantages of the invention will be apparent from the detailed description of the invention and the appended claims.

#### DETAILED DESCRIPTION OF THE INVENTION

As used in the present invention, the term "fluid" denotes gas, liquid, vapor, or combinations thereof. The term "palladium" refers to palladium in any form including, but not limited to, palladium metal and palladium oxide. The term "silver" refers to silver in any form including, but not limited to, silver metal and silver oxide. The term "substantial" or "substantially" generally means more than trivial. The term "saturated hydrocarbon" refers to any hydrocarbon which does not contain any carbon-to-carbon double bonds or carbon-to-carbon triple bonds. Examples of saturated hydrocarbons include, but are not limited to, ethane, propane, butanes, pentanes, hexanes, octanes, decanes, naphtha, and the like and combinations thereof.

The term "highly unsaturated hydrocarbon" refers to a hydrocarbon having one (or more) triple bond(s) or two or more double bonds between carbon atoms in the molecule. Examples of highly unsaturated hydrocarbons include, but are not limited to, aromatic compounds such as benzene and naphthalene; alkynes such as acetylene, propyne (also referred to as methylacetylene), and butynes; diolefins such as propadiene, butadienes, pentadienes (including isoprene), hexadienes, octadienes, and decadienes; and the like and combinations thereof.

The term "less unsaturated hydrocarbon" refers to a hydrocarbon in which the one (or more) carbon-to-carbon triple bond(s) in a highly unsaturated hydrocarbon is (are) hydrogenated to a carbon-to-carbon double bond(s), or a hydrocarbon in which the number of carbon-to-carbon double bonds is one less, or at least one less, than that in a highly unsaturated hydrocarbon, or a hydrocarbon having at least one carbon-to-carbon double bond. Examples of less unsaturated hydrocarbons include, but are not limited to, monoolefins such as ethylene, propylene, butenes, pentenes, hexenes, octenes, decenes, and the like and combinations thereof.

The term "hydrogenation process" refers to a process which hydrogenates a highly unsaturated hydrocarbon to a less unsaturated hydrocarbon or a saturated hydrocarbon. The term "selective" refers to such hydrogenation process

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in which a highly unsaturated hydrocarbon is hydrogenated to a less unsaturated hydrocarbon without further hydrogenating the less unsaturated hydrocarbon to a saturated hydrocarbon. Thus, for example, when a highly unsaturated hydrocarbon is hydrogenated to a less unsaturated hydrocarbon without further hydrogenating  
5 such less unsaturated hydrocarbon to a saturated hydrocarbon, the hydrogenation process is "more selective" than when such highly unsaturated hydrocarbon is hydrogenated to a less unsaturated hydrocarbon and then further hydrogenated to a saturated hydrocarbon.

The term "skin" refers to the exterior surface of the catalyst  
10 composition which can contain components, such as palladium, of the catalyst composition. The skin can be any thickness as long as such thickness can promote the hydrogenation process(es) disclosed herein.

According to the first embodiment of this invention, a catalyst  
composition which can be used to selectively hydrogenate a highly unsaturated  
15 hydrocarbon to a less unsaturated hydrocarbon is provided. The catalyst composition comprises (a) palladium (b) an inorganic support, and (c) a catalyst component comprising silver and an alkali metal compound wherein the palladium can be present as a "skin" on or near the surface of the catalyst composition and the silver and alkali metal compound can be distributed as a skin with the palladium or  
20 throughout the composition. The catalyst composition can further comprise a halide, preferably of a non-alkali metal halide, which can be distributed as a skin with the palladium or throughout the composition.

Generally, the thickness of the skin can be any thickness which is effective in selectively hydrogenating a highly unsaturated hydrocarbon to a less  
25 unsaturated hydrocarbon. Generally, such thickness can be in the range of from about 1 micron to about 1000 microns, preferably in the range of from about 5 microns to about 900 microns, and more preferably in the range of from about 5 microns to about 800 microns.

Various skin catalysts have been developed. See for example U.S.  
30 Patent No. 4,404,124 and divisional U.S. Patent No. 4,484,015, disclosures of which are incorporated herein by reference.

One can use any suitable method to determine the concentration of

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the palladium in the skin of the catalyst composition. Determining the concentration of the palladium in the skin of the catalyst composition also helps in determining the thickness of the skin. One technique currently favored is the electron microprobe which is known to one skilled in the art. Another technique involves breaking open a representative sample of the catalyst composition (in catalyst particle form) and treating the catalyst particles with a dilute solution of N,N-dimethyl-para-nitrosoaniline in acetone or alcohol. The treating solution reacts with the palladium to give a red color which can be used to evaluate the distribution of the palladium.

10                   Generally, palladium can be present in the catalyst composition in any weight percent so long as the palladium is substantially concentrated as a skin on or near the surface of the catalyst composition and that such weight percent is effective in selectively hydrogenating a highly unsaturated hydrocarbon to a less unsaturated hydrocarbon. Generally, the catalyst composition comprises palladium  
15 in the range of from about 0.0001 to about 3 weight percent palladium (as palladium metal) based on the total weight of the catalyst composition, preferably in the range of from about 0.0005 to about 1.5 weight percent palladium (as palladium metal) and, more preferably, in the range of from 0.001 to 1.0 weight percent palladium (as palladium metal).

20                   The catalyst composition additionally comprises a catalyst component comprising silver and an alkali metal compound. Silver can be present in the catalyst composition in any weight percent as long as such weight percent is effective in selectively hydrogenating a highly unsaturated hydrocarbon to a less unsaturated hydrocarbon and is effective in improving the operability of such  
25 catalyst composition in such selective hydrogenation compared to catalyst compositions which do not contain silver. Generally, the catalyst composition comprises silver in the range of from about 0.0003 to about 0.06 weight percent silver (as silver metal) based on the total weight of the catalyst composition, preferably in the range of from about 0.0005 to about 0.02 weight percent silver (as  
30 silver metal), more preferably in the range of from about 0.0005 to about 0.009 weight percent silver (as silver metal) and, most preferably, in the range of from 0.001 to 0.005 weight percent silver (as silver metal).

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In addition to silver, the catalyst component additionally comprises an alkali metal compound. An alkali metal compound can be present in the catalyst composition in any weight percent as long as such weight percent is effective in selectively hydrogenating a highly unsaturated hydrocarbon to a less unsaturated hydrocarbon and is effective in improving the operability of such catalyst composition in such selective hydrogenation compared to catalyst compositions which do not contain an alkali metal compound. Generally, the catalyst composition comprises an alkali metal compound in the range of from about 0.001 to about 10 weight percent alkali metal based on the total weight of the catalyst composition, preferably in the range of from about 0.005 to about 5 weight percent alkali metal and, more preferably, in the range of from 0.01 to 2 weight percent alkali metal.

The catalyst composition can additionally comprise a halide. Preferably, such halide is of a non-alkali metal halide. Such halide can be present in the catalyst composition in any weight percent as long as such weight percent is effective in selectively hydrogenating a highly unsaturated hydrocarbon to a less unsaturated hydrocarbon. Generally, when such halide, preferably of a non-alkali metal halide, is present, the catalyst composition comprises a halide in the range of from about 0.001 to about 10 weight percent halide based on the total weight of the catalyst composition, preferably in the range of from about 0.005 to about 5 weight percent halide and, more preferably, in the range of from 0.01 to 2 weight percent halide. Preferably, such halide is fluoride.

When a catalyst composition is prepared according to the inventive process(es) disclosed herein and comprises palladium, an inorganic support, a catalyst component comprising silver and an alkali metal compound, and, optionally, a halide of a non-alkali metal halide and is utilized in the hydrogenation of a highly unsaturated hydrocarbon to a less unsaturated hydrocarbon, there is an increased or enhanced selectivity to a desired product such as a less unsaturated hydrocarbon when compared to a catalyst composition prepared by methods other than the inventive process(es) disclosed herein.

The catalyst composition can be fresh or it can be a used and thereafter oxidatively regenerated catalyst composition. The catalyst composition



can have any suitable shape such as spherical, cylindrical, trilobal, or combinations thereof. The preferred shape is either spherical or cylindrical. The particles of the catalyst composition generally have a size in the range of from about 0.5 millimeters (mm) to about 10 mm, preferably in the range of from about 1 mm to about 8 mm and, more preferably, in the range of from 1 mm to 7 mm. Generally the surface area of the catalyst composition is in the range of from about 1 m<sup>2</sup>/g (measured by the Brunauer, Emmett, and Teller method, i.e., BET method) to about 200 m<sup>2</sup>/g, preferably in the range of from about 1 m<sup>2</sup>/g to about 150 m<sup>2</sup>/g, more preferably in the range of from about 2 m<sup>2</sup>/g to about 125 m<sup>2</sup>/g and, most preferably, in the range of from 2 m<sup>2</sup>/g to 80 m<sup>2</sup>/g.

The catalyst composition can be prepared by any suitable method(s) or means which results in the palladium concentrated in the exterior surface skin of the catalyst composition with a catalyst component comprising silver and an alkali metal compound distributed in the skin or throughout the catalyst composition and, if desired, a halide (preferably of a non-alkali metal halide) distributed in the skin or throughout the catalyst composition. The catalyst composition components of palladium and a catalyst component comprising silver and an alkali metal compound (preferably potassium fluoride) and, if present, a halide, can be deposited onto and/or incorporated into or with the inorganic support (preferably alumina) by any suitable means and in any suitable order which results in a catalyst composition comprising catalyst composition components in the weight percent ranges disclosed herein.

The palladium can be incorporated (e.g., by ion exchange or impregnation) into, onto, or with the inorganic support, preferably alumina. A preferred palladium impregnation utilizes an incipient wetness impregnation technique in which a solution of the incorporating element(s) is used to essentially completely fill the pores of a substrate material (such as an inorganic support). The inorganic support can also be sprayed with an impregnating solution comprising a palladium compound. Generally, the concentration of the palladium compound in the impregnating solution can be any concentration that can produce a catalyst composition comprising palladium in the weight percent ranges disclosed herein. Preferably, the solvent of the impregnating solution is water or an alcohol such as

ethanol or mixtures thereof. The weight ratio of the impregnating solution comprising a palladium compound to the inorganic support can be any ratio that can produce a catalyst composition comprising palladium in the weight percent ranges disclosed herein.

5                   For example, an inorganic support (preferably alumina) is impregnated with at least one Pd compound (such as  $\text{H}_2\text{PdCl}_4$ ) to obtain a palladium-impregnated material, the impregnated material is then dried under a composition drying condition as described herein to obtain a dried material, and then heated (calcined) under a composition calcining condition as described herein  
10 to obtain a dried and calcined palladium/inorganic support composition. The palladium/inorganic support composition can then be contacted with a solution (preferably aqueous) of at least one silver compound (i.e., a silver-containing solution), preferably silver nitrate, and a solution of an alkali metal compound (i.e., an alkali metal compound-containing solution), preferably potassium fluoride,  
15 followed by drying under a composition drying condition as described herein to obtain a dried material, and then heating (calcining) under a composition calcining condition as described herein to thereby obtain a catalyst composition of this invention comprising palladium, silver, and alkali metal in the weight percent ranges disclosed herein.

20                   In another preparation method, the palladium/inorganic support composition can be contacted with a solution (preferably aqueous) of a silver compound (i.e., a silver-containing solution) followed by drying under a composition drying condition as described herein to obtain a dried material, and then heating (calcining) under a composition calcining condition as described herein  
25 to thereby obtain a palladium/silver/inorganic support composition. Such palladium/silver/inorganic support composition can then be contacted with a solution of an alkali metal compound (i.e., an alkali metal compound-containing solution) followed by drying under a composition drying condition as described herein to obtain a dried material, and then heating (calcining) under a composition calcining  
30 condition as described herein to thereby obtain a catalyst composition of this invention comprising palladium, silver, and alkali metal in the weight percent ranges disclosed herein.

In addition, an alkali metal compound (or an alkali metal compound-containing solution) can be incorporated (e.g., by impregnation or spraying) with an inorganic support (preferably alumina) before such support is incorporated with a suitable palladium compound (or a palladium-containing solution) and a suitable silver compound (or a silver-containing solution). Alternatively, an alkali metal compound can be incorporated (e.g., by impregnation or spraying) with an inorganic support simultaneously with or after the incorporation with a suitable palladium compound. Also, an alkali metal compound can be incorporated with the inorganic support between the palladium and silver incorporation steps or after the palladium and silver incorporation steps.

When the catalyst composition further comprises a halide, preferably of a non-alkali metal halide, such halide can be incorporated with the palladium/inorganic support composition in any suitable manner and in any suitable order which results in a catalyst composition of this invention comprising halide in the weight percent ranges disclosed herein. Preferably, such halide is fluoride. Preferably, such non-alkali metal halide is a non-alkali metal fluoride selected from the group consisting of HF,  $\text{NH}_4\text{F}$ ,  $\text{NH}_4\text{HF}_2$ , and the like and combinations thereof. More preferably, such non-alkali metal halide is  $\text{NH}_4\text{F}$ . The inorganic support can be incorporated, preferably impregnated, with a halide (preferably of a non-alkali metal fluoride, more preferably  $\text{NH}_4\text{F}$ ) preferably together with an alkali metal compound.

After the incorporation of the inorganic support with palladium, a catalyst component comprising silver and an alkali metal compound, and, optionally, a halide has been completed as described herein, the thus-obtained material is dried under a composition drying condition as described herein and then calcined under a composition calcining condition as described herein. Optionally, the calcined material can then be reduced with hydrogen gas preferably at a temperature in the range of from about  $30^\circ\text{C}$  to about  $300^\circ\text{C}$  for a time period in the range of from about 0.1 hour to about 20 hours.

In a preferred catalyst composition preparation, a supported palladium/silver/alumina catalyst material obtained by the method disclosed in U.S. Patent 4,404,124 and divisional U.S. Patent 4,484,015 is impregnated with an

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aqueous solution of an alkali metal halide (preferably potassium fluoride) followed by drying under a composition drying condition as described herein and then calcined under a composition calcining condition as described herein. In another preferred catalyst composition preparation, a supported palladium/silver/alumina catalyst material obtained by the method disclosed in U.S. Patent 4,404,124 and divisional U.S. Patent 4,484,015 is co-impregnated with an aqueous solution of an alkali metal halide (preferably potassium fluoride) and a non-alkali metal halide (preferably a non-alkali metal fluoride, more preferably  $\text{NH}_4\text{F}$ ) followed by drying under a composition drying condition as described herein and then calcined under a composition calcining condition as described herein.

Generally, the concentrations of a silver compound and an alkali metal compound, and optionally a halide (preferably of a non-alkali metal halide), in the contacting solution(s) (preferably aqueous) can be any concentrations that can produce a catalyst composition disclosed herein. The preferred silver contacting method is by soaking, i.e., the volume of silver compound-containing solution is in excess of the pore volume of the inorganic support. The preferred alkali metal compound contacting method and halide (preferably of a non-alkali metal halide) contacting method is "incipient wetness impregnation," i.e., essentially completely filling the pores of an inorganic support with an alkali metal compound-containing solution and, if desired, a halide-containing solution. Generally, the weight ratio of a silver-containing compound solution and an alkali metal compound-containing solution and, optionally, a halide-containing solution, to the inorganic support can be any ratio that can produce a catalyst composition comprising silver and alkali metal, and, if desired, a halide (preferably of a non-alkali metal halide) in the weight percent ranges disclosed herein. The impregnated material can then be dried under a composition drying condition as described herein followed by calcining under a composition calcining condition as described herein to obtain a catalyst composition of this invention.

Generally, a composition drying condition, as referred to herein, includes a temperature in the range of from about  $35^\circ\text{C}$  to about  $290^\circ\text{C}$ , preferably in the range of from about  $40^\circ\text{C}$  to about  $280^\circ\text{C}$  and, more preferably, in the range of from  $45^\circ\text{C}$  to  $275^\circ\text{C}$ . Such composition drying condition includes a time period

for conducting such drying generally in the range of from about 0.1 hour to about 6 hours, preferably in the range of from about 0.15 hour to about 5 hours and, more preferably, in the range of from 0.2 hour to 4 hours. Generally, the composition can be dried at any suitable pressure. Preferably, such composition drying condition  
5 includes a pressure in the range of from about atmospheric (i.e. about 101.2 kPa to about 689 kPa, (about 14.7 pounds per square inch absolute) to about 100 pounds per square inch absolute (psia)), more preferably about atmospheric.

Generally a composition calcining condition, as referred to herein, includes calcining of the composition either in air or in a non-oxidizing gas  
10 atmosphere at a temperature in the range of from about 200°C to about 900°C, preferably at a temperature in the range of from about 250°C to about 750°C and, more preferably, at a temperature in the range of from 350°C to 600°C. Such composition calcining condition generally includes a time period in the range of from about 0.5 hour to about 40 hours, preferably for a time period in the range of  
15 from about 0.75 hour to about 30 hours and, more preferably, for a time period in the range of from 1 hour to 20 hours. Such composition calcining condition generally includes a pressure in the range of from about 48 kPa to about 5.167 MPa (about 7 pounds per square inch absolute (psia) to about 750 psia), preferably in the range of from about 48 kPa to about 3.10 MPa (about 7 psia to about 450 psia) and,  
20 more preferably, in the range of from 48 kPa to 1.03 MPa (7 psia to 150 psia).

Examples of suitable palladium compounds which can be used in preparing a catalyst composition of this invention include, but are not limited to, palladium bromide, palladium chloride, palladium iodide, palladium nitrate, palladium nitrate hydrate, tetraammine palladium nitrate, palladium oxide, palladium  
25 oxide hydrate, palladium sulfate, and the like and combinations thereof. The palladium can have any available oxidation state. The presently preferred palladium compound is palladium chloride. More preferably, hydrochloric acid is added to such palladium chloride ( $\text{PdCl}_2$ ) to form a  $\text{PdCl}_4^{-2}$  complex. When added to the support by impregnation from solution, some of the compounds can be added from  
30 aqueous solution, but others will require non-aqueous solvents such as alcohols, hydrocarbons, ethers, ketones and the like.

Examples of suitable silver compounds which can be used in

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preparing a catalyst composition of this invention include, but are not limited to, silver nitrate, silver acetate, silver cyanide and the like and combinations thereof. The presently preferred silver compound is silver nitrate.

5 Examples of suitable alkali metal compounds which can be used in preparing a catalyst composition of this invention include, but are not limited to, alkali metal halides, alkali metal hydroxides, alkali metal carbonates, alkali metal bicarbonates, alkali metal nitrates, alkali metal carboxylates, and the like and combinations thereof. Preferably, the alkali metal compound is an alkali metal halide, more preferably the alkali metal compound is an alkali metal iodide or an  
10 alkali metal fluoride. Generally, the alkali metal of such alkali metal compound is selected from the group consisting of potassium, rubidium, cesium, and the like and combinations thereof. Preferably, the alkali metal of such alkali metal compound is potassium. Most preferably, the alkali metal compound is potassium fluoride (KF).

Further examples of suitable alkali metal compounds include, but are  
15 not limited to, sodium fluoride, lithium fluoride, rubidium fluoride, cesium fluoride, sodium iodide, potassium iodide, lithium iodide, rubidium iodide, cesium iodide, sodium chloride, potassium chloride, lithium chloride, rubidium chloride, cesium chloride, sodium bromide, potassium bromide, lithium bromide, rubidium bromide, cesium bromide, sodium hydroxide, potassium hydroxide, lithium hydroxide,  
20 rubidium hydroxide, cesium hydroxide, sodium oxide, potassium oxide, lithium oxide, rubidium oxide, cesium oxide, sodium carbonate, potassium carbonate, lithium carbonate, rubidium carbonate, cesium carbonate, sodium nitrate, potassium nitrate, lithium nitrate, rubidium nitrate, cesium nitrate, and the like and combinations thereof.

25 Examples of a suitable inorganic support include, but are not limited to, alumina, silica, zirconia, titania, an aluminosilicate (such as clays and/or zeolites), a spinel such as zinc aluminate, calcium aluminate, and magnesium aluminate, zinc titanate, and the like and combinations thereof.

The preferred inorganic support is any suitable alumina such as, but  
30 not limited to, alpha alumina, beta alumina, delta alumina, eta alumina, gamma alumina, theta alumina, and the like and combinations thereof. Preferably, such alumina is alpha alumina. The alumina can also contain minor amounts of other

ingredients, such as, for example, silica in a range of from about 1 weight percent silica to about 10 weight percent silica, which do not adversely affect the quality of the inorganic support. Generally, it is desirable to have an essentially pure alumina, preferably essentially pure alpha alumina, as the inorganic support. The alumina  
5 can be made by any manner or method(s) known in the art. The alumina can have any surface area, pore volume, average pore diameter, and particle size which can produce the catalyst composition as disclosed herein.

According to the second embodiment of this invention, a hydrogenation process is provided. The hydrogenation process of this invention  
10 comprises contacting a hydrocarbon-containing fluid which comprises one or more highly unsaturated hydrocarbon(s) with a catalyst composition disclosed herein in the presence of hydrogen in a hydrogenation zone under a hydrogenation condition effective to hydrogenate such one or more highly unsaturated hydrocarbon(s) to a less unsaturated hydrocarbon. Such hydrogenation process can be conducted in the  
15 presence or absence of a sulfur impurity such as a sulfur compound.

Hydrogen can be present either in the hydrocarbon-containing fluid or in a hydrogen-containing fluid which is mixed with the hydrocarbon-containing fluid before contacting with a catalyst composition disclosed herein. If a hydrogen-containing fluid is used, it can be a substantially pure hydrogen or any fluid  
20 containing a sufficient concentration of hydrogen to effect the hydrogenation disclosed herein. It can also contain other gases such as, for example, nitrogen, methane, carbon monoxide, carbon dioxide, steam, or combinations thereof so long as the hydrogen-containing fluid contains a sufficient concentration of hydrogen to effect the hydrogenation disclosed herein.

25 Optionally, the catalyst composition can be first treated, prior to the hydrogenation disclosed herein, with a hydrogen-containing fluid to activate the catalyst composition. Such reductive, or activation, treatment can be carried out at a temperature generally in the range of from about 20°C to about 400°C, preferably in the range of from about 30°C to about 200°C for a time period in the range of  
30 from about 1 minute to about 30 hours, preferably in the range of from about 0.5 hour to about 25 hours and, more preferably, in the range of from 1 hour to 20 hours at a pressure generally in the range of from about 6.89 kPa to about 6890 kPa

(about 1 pound per square inch absolute to about 1000 pounds per square inch absolute (psia)), preferably in the range of from about 101.2 kPa to about 3445 kPa (about 14.7 psia to about 500 psia) and, more preferably, in the range of from 413 kPa to 1378 kPa (60 psia to 200 psia). During this reductive treatment, palladium and silver compounds which may be present in the catalyst composition after the composition calcining step described herein are substantially reduced to palladium and silver. When this optional reductive treatment is not carried out, the hydrogen gas present in the reaction medium accomplishes this reduction during the initial phase of the hydrogenation process(es) disclosed herein.

10           The highly unsaturated hydrocarbon(s) is present in the hydrocarbon-containing fluid as an impurity generally at a level found in typical commercial feed streams. The highly unsaturated hydrocarbon(s) is present in the hydrocarbon-containing fluid generally in the range of from about 1 part highly unsaturated hydrocarbon(s) per billion parts hydrocarbon-containing fluid by weight (i.e., about 15   1 ppb) to about 50 weight percent, typically at a level in the range of from about 10 ppb to about 30 weight percent and, more typically, at a level in the range of from 20 ppb to 20 weight percent.

          The hydrocarbon-containing fluid of the hydrogenation process(es) of this invention can also comprise one or more less unsaturated hydrocarbon(s) such as a monoolefin(s) and one or more saturated hydrocarbon(s) such as an alkane(s). 20   These additional hydrocarbons can be present in the hydrocarbon-containing fluid at a level in the range of from about 0.001 weight percent to about 99.999 weight percent.

          Examples of suitable alkynes include, but are not limited to, 25   acetylene, propyne (also referred to as methylacetylene), 1-butyne, 2-butyne, 1-pentyne, 2-pentyne, 3-methyl-1-butyne, 1-hexyne, 1-heptyne, 1-octyne, 1-nonyne, 1-decyne, and the like and combinations thereof. The presently preferred alkynes are acetylene and propyne.

          The alkynes are preferably hydrogenated to the corresponding 30   alkenes. For example, acetylene is hydrogenated to ethylene; propyne is hydrogenated to propylene; and the butynes are hydrogenated to the corresponding butenes (e.g., 1-butene, 2-butenes).



Examples of suitable diolefins include those containing in the range of from 3 carbon atoms per molecule to about 12 carbon atoms per molecule. Such diolefins include, but are not limited to, propadiene, 1,2-butadiene, 1,3-butadiene, isoprene, 1,2-pentadiene, 1,3-pentadiene, 1,4-pentadiene, 1,2-hexadiene, 1,3-hexadiene, 1,4-hexadiene, 1,5-hexadiene, 2-methyl-1,2-pentadiene, 2,3-dimethyl-1,3-butadiene, heptadienes, methylhexadienes, octadienes, methylheptadienes, dimethylhexadienes, ethylhexadienes, trimethylpentadienes, methyloctadienes, dimethylheptadienes, ethyloctadienes, trimethylhexadienes, nonadienes, decadienes, undecadienes, dodecadienes, cyclopentadienes, cyclohexadienes, methylcyclopentadienes, cycloheptadienes, methylcyclohexadienes, dimethylcyclopentadienes, ethylcyclopentadienes, dicyclopentadiene (also known as tricyclo[5.2.1]<sup>2,6</sup>deca-3,8-diene), and the like and combinations thereof.

Presently preferred diolefins are propadiene, 1,2-butadiene, 1,3-butadiene, pentadienes (such as 1,3-pentadiene, 1,4-pentadiene, isoprene), cyclopentadienes (such as 1,3-cyclopentadiene) and dicyclopentadiene (also known as tricyclo[5.2.1]<sup>2,6</sup>deca-3,8-diene). These diolefins are preferably hydrogenated to their corresponding monoolefins containing the same number of carbon atoms per molecule as the diolefins. For example, propadiene is hydrogenated to propylene; 1,2-butadiene and 1,3-butadiene are hydrogenated to 1-butene and 2-butene; 1,3-pentadiene and 1,4-pentadiene are hydrogenated to 1-pentene and 2-pentene; isoprene is hydrogenated to methyl-1-pentenenes and methyl-2-pentenenes; and 1,3-cyclopentadiene is hydrogenated to cyclopentene.

Examples of aromatic hydrocarbons which may be present in the hydrocarbon-containing fluid include, but are not limited to, benzene, toluene, ethylbenzene, styrene, xylenes, and the like and combinations thereof.

Examples of suitable monoolefins include, but are not limited to, ethylene, propylene, 1-butene, 2-butene, isobutylene, 1-pentene, 2-pentene, methyl-1-butenes (such as 2-methyl-1-butene), methyl-2-butenes (such as 2-methyl-2-butene), 1-hexene, 2-hexene, 3-hexene, methyl-1-pentenenes, 2,3-dimethyl-1-butene, 1-heptene, 2-heptene, 3-heptene, methyl-1-hexenenes, methyl-2-hexenenes, methyl-3-hexenenes, dimethylpentenenes, ethylpentenenes, octenenes, methylheptenenes, dimethylhexenenes, ethylhexenenes, nonenenes, methyloctenenes, dimethylheptenenes, ethylheptenenes,

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trimethylhexenes, cyclopentene, cyclohexene, methylcyclopentene, cycloheptene, methylcyclohexene, dimethylcyclopentenes, ethylcyclopentenes, cyclooctenes, methylcycloheptenes, dimethylcyclohexenes, ethylcyclohexenes, trimethylcyclohexenes, methylcyclooctenes, dimethylcyclooctenes, ethylcyclooctenes, and the like  
5 and combinations thereof.

Examples of suitable saturated hydrocarbons include, but are not limited to, methane, ethane, propane, butane, methylpropane, methylbutane, dimethylbutane, pentanes, hexanes, and the like and combinations thereof.

Furthermore, the hydrocarbon-containing fluid can generally contain  
10 in the range of from about 0.001 weight percent hydrogen to about 20 weight percent hydrogen, preferably in the range of from about 0.001 weight percent hydrogen to about 15 weight percent hydrogen, and up to 10,000 parts per million by volume (ppmv) of carbon monoxide.

Examples of a sulfur compound(s) which can be present during the  
15 hydrogenation process(es) disclosed herein as a sulfur impurity, usually contained in the hydrocarbon-containing fluid, include, but are not limited to, hydrogen sulfide, carbonyl sulfide (COS), carbon disulfide (CS<sub>2</sub>), mercaptans (RSH), organic sulfides (R-S-R), organic disulfides (R-S-S-R), thiophene, substituted thiophenes, organic trisulfides, organic tetrasulfides, and the like and combinations thereof, wherein each  
20 R can be an alkyl or cycloalkyl or aryl group containing 1 carbon atom to 10 carbon atoms. It is within the scope of this invention to have additional compounds (such as water, alcohols, ethers, aldehydes, ketones, carboxylic acids, esters and other oxygenated compounds) present in the hydrocarbon-containing fluid as long as such additional compounds do not significantly interfere with the hydrogenation  
25 process(es) disclosed herein.

Generally, the sulfur compound(s) are present in the hydrocarbon-containing fluid in trace amounts preferably at a concentration of less than about 1000 parts per million by volume (ppmv) based on the total volume of the hydrocarbon-containing fluid, and preferably at a concentration in the range of from  
30 about 0.5 ppbv sulfur to about 1000 ppmv sulfur (i.e., about 0.5 part sulfur per billion parts hydrocarbon-containing fluid by volume to about 1000 parts sulfur per million parts hydrocarbon-containing fluid by volume), more preferably at a

concentration in the range of from about 1 ppbv sulfur to about 500 ppmv sulfur and, most preferably, in the range of from 1 ppbv sulfur to 300 ppmv sulfur.

The hydrogenation process(es) of this invention is generally carried out by contacting a hydrocarbon-containing fluid comprising at least one highly unsaturated hydrocarbon with a catalyst composition of this invention in the presence of hydrogen under a hydrogenation condition. The hydrocarbon-containing fluid can be contacted by any suitable manner with the catalyst composition described herein which is contained within a hydrogenation zone. Such hydrogenation zone can comprise, for example, a reactor vessel.

The contacting step, of contacting the hydrocarbon-containing fluid with the catalyst composition disclosed herein, can be operated as a batch process step or, preferably, as a continuous process step. In the latter operation, a solid or fixed catalyst bed or a moving catalyst bed or a fluidized catalyst bed can be employed. Preferably, a fixed catalyst bed is employed. Any of these operational modes have advantages and disadvantages, and those skilled in the art can select the one most suitable for a particular hydrocarbon-containing fluid and catalyst composition.

The contacting step is preferably carried out within a hydrogenation zone, wherein is contained the catalyst composition disclosed herein, and under a hydrogenation condition that suitably promotes the hydrogenation process of a highly unsaturated hydrocarbon to a less unsaturated hydrocarbon as described herein. Such hydrogenation condition should be such as to avoid significant hydrogenation of a less unsaturated hydrocarbon(s) being initially present in the hydrocarbon-containing fluid to a saturated hydrocarbon(s) such as an alkane(s) or cycloalkane(s).

Generally, such hydrogenation condition comprises a temperature and a pressure necessary for the hydrogenation process(es) of this invention depending largely upon the activity of the catalyst composition, the hydrocarbon-containing fluid, and the desired extent of hydrogenation. Generally, such temperature is in the range of from about 10°C to about 300°C, preferably in the range of from about 20°C to about 250°C and, most preferably, in the range of from 20°C to 200°C. A suitable pressure is generally in the range of from about 136 kPa to about 13.88

If it is desired to regenerate a catalyst composition of this invention after prolonged use in the hydrogenation process(es) described herein, the regeneration can be accomplished by calcining the catalyst composition in an oxidizing atmosphere such as in air at a temperature that does not exceed about 600°C to burn off carbonaceous and sulfur deposits. Optionally, the catalyst composition can be reimpregnated with palladium and a catalyst component comprising silver and an alkali metal compound and, if desired, a halide of a non-alkali metal halide, and then dried and calcined as described herein for the production of a fresh catalyst composition of this invention.

30 EXAMPLE I

This example illustrates the preparation of various palladium-containing catalyst compositions to be used in a hydrogenation process.

Catalyst A (Invention) was prepared in the following manner. Silver, potassium, and fluoride were added to a commercial Pd/Al<sub>2</sub>O<sub>3</sub> catalyst containing about 0.02 weight % Pd and having a surface area of about 3 to 5 m<sup>2</sup>/g available from United Catalyst Inc. (UCI), Louisville, Kentucky under the product designation of "G83A". Silver was first added by incipient wetness (i.e., essentially completely filling the pores of a substrate material with a solution of the incorporating elements). A solution of 0.008 gram of AgNO<sub>3</sub> dissolved in 22 mL of distilled water was added to a 100 gram quantity of the commercial Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. The resulting Pd/Ag/Al<sub>2</sub>O<sub>3</sub> catalyst was then dried in air at approximately 275°C for about 1 hour and then calcined in air at about 538°C for about 3 hours. Potassium and fluoride were then added by incipient wetness. A solution of 0.117 gram of KF and 0.0555 gram of NH<sub>4</sub>HF<sub>2</sub> dissolved in 5.5 mL of distilled water was added to a 25 gram quantity of the Pd/Ag/Al<sub>2</sub>O<sub>3</sub> catalyst. The resulting Pd/Ag/K/F/Al<sub>2</sub>O<sub>3</sub> catalyst was then dried in air at approximately 275°C for about 1.5 hours and then calcined in air at about 538°C for about 3 hours to thereby provide Invention Catalyst A. Invention Catalyst A contained about 0.02 weight % Pd, about 0.005 weight % Ag, about 0.3 weight % K, and about 0.3 weight % F.

#### Catalyst B (Control)

Was a Pd/Ag/K/F/Al<sub>2</sub>O<sub>3</sub> catalyst which was prepared in a manner similar to the above-described Invention Catalyst A. Control Catalyst B contained about 0.02 weight % Pd, about 0.02 weight % Ag, about 0.3 weight % K, and about 0.3 weight % F.

#### Catalyst C (Control)

Was a Pd/Ag/K/F/Al<sub>2</sub>O<sub>3</sub> catalyst which was prepared in a manner similar to the above-described Invention Catalyst A. Control Catalyst C contained about 0.02 weight % Pd, about 0.06 weight % Ag, about 0.3 weight % K, and about 0.3 weight % F.

#### Catalyst D (Invention)

Was prepared in the following manner. A Pd/Al<sub>2</sub>O<sub>3</sub> catalyst containing about 0.025 weight % Pd and having a surface area of about 7 to 8 m<sup>2</sup>/g was prepared by soaking 200 grams of a commercially available alumina (Al<sub>2</sub>O<sub>3</sub>) support in the form of 7/32 inch by 7/32 inch pellets (such alumina support had

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been provided by United Catalyst Inc. (UCI)) for about 1 hour in a solution containing 0.050 gram of palladium (in the form of  $\text{H}_2\text{PdCl}_4$ ) dissolved in 200 mL of distilled water. The catalyst pills were stirred several times over the hour to ensure an even distribution of Pd. At the end of the hour, the clear solution was decanted off. The resulting  $\text{Pd}/\text{Al}_2\text{O}_3$  catalyst was then dried in air at  $120^\circ\text{C}$  for about 1 hour and then calcined in air at  $538^\circ\text{C}$  for about 3 hours to thereby provide a  $\text{Pd}/\text{Al}_2\text{O}_3$  catalyst. Silver was then added to the  $\text{Pd}/\text{Al}_2\text{O}_3$  catalyst by soaking a 25 gram quantity of the  $\text{Pd}/\text{Al}_2\text{O}_3$  catalyst in a solution of 0.00495 gram of Ag (as  $\text{AgNO}_3$ ) in 25 mL of distilled water for 1 hour. The catalyst pills were stirred several times over the hour to ensure an even distribution of Ag. At the end of the hour, the solution was decanted off. The resulting  $\text{Pd}/\text{Ag}/\text{Al}_2\text{O}_3$  catalyst was then dried in air at  $120^\circ\text{C}$  for about 1 hour and then calcined in air at  $538^\circ\text{C}$  for about 3 hours. Potassium was then added by incipient wetness. A solution of 0.037 gram KF dissolved in 6.2 mL of distilled water was added to a 25 gram quantity of the  $\text{Pd}/\text{Ag}/\text{Al}_2\text{O}_3$  catalyst. The resulting  $\text{Pd}/\text{Ag}/\text{K}/\text{F}/\text{Al}_2\text{O}_3$  catalyst was then dried in air at  $120^\circ\text{C}$  for about 1 hour and then calcined in air at  $538^\circ\text{C}$  for about 3 hours to thereby provide Invention Catalyst D. Invention Catalyst D contained about 0.025 weight % Pd, about 0.01 weight % Ag, about 0.1 weight % K, and about 0.05 weight % F.

20

Catalyst E (Control)

Was prepared in a manner similar to the above-described Invention Catalyst D, except the silver was added in a manner similar to the above-described Invention Catalyst A. Control Catalyst E contained about 0.025 weight % Pd, about 0.04 weight % Ag, about 0.1 weight % K, and about 0.05 weight % F.

25

Catalyst F (Invention)

Was prepared in the following manner. Silver, potassium, and fluoride were added to a commercial  $\text{Pd}/\text{Al}_2\text{O}_3$  catalyst containing about 0.02 weight % Pd and having a surface area of about 3 to 5  $\text{m}^2/\text{g}$  available from United Catalyst Inc. (UCI), Louisville, Kentucky under the product designation of "G83A". Silver was first added to the  $\text{Pd}/\text{Al}_2\text{O}_3$  catalyst in a manner similar to the above-described Invention Catalyst A. The potassium and fluoride were then added to the catalyst in a manner similar to the above-described Invention Catalyst A except that  $\text{NH}_4\text{F}$  was

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used as the F source instead of  $\text{NH}_4\text{HF}_2$ . Invention Catalyst F contained about 0.02 weight % Pd, about 0.005 weight % Ag, about 0.5 weight % K, and about 0.5 weight % F.

#### Catalyst G (Control)

5                   Was prepared in a manner similar to Invention Catalyst F. Control Catalyst G contained about 0.02 weight % Pd, about 0.06 weight % Ag, about 0.5 weight % K, and about 0.5 weight % F.

#### EXAMPLE II

10                   This example illustrates the performance of the catalysts described hereinabove in Example I in a hydrogenation process.

                  About 23 grams (i.e., about 20 cc) of each of the above described catalysts were placed in a stainless steel reactor tube having a 0.62 inch inner diameter and a length of about 18 inches. The catalyst (resided in the middle of the reactor; both ends of the reactor were packed with 6 mL of 3 mm glass beads) was  
15                   reduced at about 38°C for about 1 hour under hydrogen gas flowing at 12 liters per hour at 200 pounds per square inch gauge (psig). Thereafter, a hydrocarbon-containing fluid, typical of a feed from a front-end depropanizer of an ethylene plant, containing approximately (all by weight unless otherwise noted) hydrogen, 2.1%; methane, 22%; ethylene, 54%; propylene, 21%; acetylene, 4300 to 5400 ppm;  
20                   propadiene, 4300 to 5400 ppm; propyne, 4300 to 5400 ppm; and carbon monoxide, 300 ppm (by volume) was then introduced into the reactor. The hydrocarbon-containing fluid and hydrogen were introduced continuously into the reactor at a rate of 900 mL per minute at 200 psig (translating to a gas hourly space velocity of about 2500  $\text{hour}^{-1}$ ). The reactor temperature was increased until the hydrogenation  
25                   was uncontrollable, i.e., the uncontrollable hydrogenation of ethylene was allowed to occur. During the uncontrollable hydrogenation of ethylene, the heat of hydrogenation built up such that the reactor temperature exceeded about 120°C (i.e., about 120°C to about 150°C). The reactor was then allowed to cool to below 38°C before data collection was started.

30                   The hydrocarbon-containing fluid and hydrogen were then continuously introduced over the catalyst at a rate of 900 mL/min at 200 psig, while holding the temperature constant before sampling the exit stream by gas

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chromatography. The reactor temperature was determined by inserting a thermocouple into the thermowell (which ran up the center of the reactor and catalyst bed) and varying its position until the highest temperature was observed. The furnace temperature was then raised a few degrees and the testing cycle was  
5 repeated.

In order to more realistically predict the performance of the above-described catalysts in a hydrogenation process that contains catalyst poisons such as sulfur impurities, the resistance of the above-described catalysts to a sulfur poison was determined by continuing the above-described testing cycle in the following  
10 manner. The reactor was heated to a temperature in the range of from about 55°C to about 85°C and a large concentration of carbonyl sulfide (COS) (approximately 300 mL at standard temperature and pressure (STP) of 5000 parts per million by volume (ppmv) COS in nitrogen) was introduced over the catalyst. COS  
15 concentrations were then regulated by substituting part of the hydrogen flow (flowing at 12 liters/hour at 200 psig) with a blend of COS and hydrogen (COS/H<sub>2</sub> blend). The flow rates were set to deliver the hydrocarbon-containing fluid, hydrogen, and COS/H<sub>2</sub> blend to obtain a concentration of 12 parts COS per million parts by volume of total feed.

The reactor was then "lined out" (i.e., acetylene and ethane  
20 concentrations remained essentially constant) at a temperature below total acetylene conversion. Next, the temperature was increased and the reactor was again allowed to line out. This "lining out" process was repeated until all the acetylene was hydrogenated or the reaction was uncontrollable. The entire run was conducted in a continuous mode, with the catalyst always having hydrocarbon-containing fluid  
25 passing over the catalyst. The reactor effluent, i.e., the product stream, was analyzed by gas chromatography.

In the results shown below in Table I, T1 is referred to as the  
"cleanup" temperature which is the temperature at which the acetylene concentration falls below 20 ppm (i.e., 20 parts acetylene per million parts hydrocarbon-containing  
30 fluid by weight). In a hydrogenation process, a low T1 is desirable. A low T1 indicates higher activity and a longer run life of the catalyst. As the catalyst is used in a hydrogenation process, operating temperatures must be steadily increased in



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time to compensate for the decrease in activity of the catalyst. However, there is an upper temperature limit (T2) above which the uncontrollable hydrogenation of ethylene to ethane will occur. Thus, a low T1 allows an overall longer run life of the catalyst. In Table I, T2 is referred to as the "runaway" temperature which is the temperature at which 3 weight % of ethane is produced (based on total hydrocarbons). In Table I,  $\Delta T$  is the difference between T2 and T1. The  $\Delta T$  is a measure of ethylene selectivity which can also be viewed as a window of operability of the reaction. The greater the temperature difference between T2 and T1 (i.e., the greater the  $\Delta T$ ) attained with a particular catalyst, the more satisfactorily the catalyst will perform as a hydrogenation catalyst composition.

In addition, in Table I "hydrocarbon selectivities at T1" refers to the molar percentage of acetylene being converted to a particular hydrocarbon. If the selectivity exceeds 100 % for a particular hydrocarbon (except ethylene) then ethylene is being consumed to make that particular hydrocarbon. In the same manner, if the selectivity to ethylene is negative, then ethylene has been consumed to produce another hydrocarbon. For example, "ethane (C<sub>2</sub>) selectivity at T1" refers to the molar percentage of acetylene that is converted to ethane at T1. Any hydrocarbon (both saturated and unsaturated) containing 4 carbon atoms per molecule is referred to as "C<sub>4</sub>". Similarly, any hydrocarbon containing 6 or more carbon atoms per molecule is referred to as "heavies". Selectivities were determined by the following equation:

$$\text{Selectivity to X} = \frac{[(\text{mole of X produced})/(\text{mole of acetylene consumed}) * \text{No. of acetylene units used to make X} * 100]}$$

TABLE I

Catalyst	Temperatures (°F)			Hydrocarbon Selectivities At T1		
	T1	T2	ΔT	C <sub>2</sub> <sup>b</sup>	C <sub>4</sub> <sup>i</sup>	Heavies <sup>j</sup>
Catalyst A (Invention) <sup>a</sup> Without COS With COS	122	164	42	21.9	15.3	7.3
	153	205	52	66.6	5.5	0.0
Catalyst B (Control) <sup>b</sup> Without COS With COS	130	173	43	12.1	13.9	9.3
	154	199	45	40.9	8.5	1.4
Catalyst C (Control) <sup>c</sup> Without COS With COS	128	172	44	17.4	14.8	7.8
	153	201	48	57.0	6.8	0.6
Catalyst D (Invention) <sup>d</sup> Without COS With COS	128	ND <sup>k</sup>	ND	14.0	11.6	8.7
	181	ND	ND	72.1	4.8	1.6
Catalyst E (Control) <sup>e</sup> Without COS With COS	131	192	61	8.1	6.3	7.0
	185	226	41	110.8	5.0	1.5
Catalyst F (Invention) <sup>f</sup> Without COS With COS	125	163	38	22.0	13.7	11.8
	ND	ND	ND	ND	ND	ND
Catalyst G (Control) <sup>g</sup> Without COS With COS	128	177	49	17.3	13.3	4.7
	169	205	36	116.3	4.7	0
<sup>a</sup>	Catalyst A (0.02 wt. % Pd / 0.005 wt. % Ag / 0.3 wt. % K / 0.3 wt. % F)					
<sup>b</sup>	Catalyst B (0.02 wt. % Pd / 0.02 wt. % Ag / 0.3 wt. % K / 0.3 wt. % F)					
<sup>c</sup>	Catalyst C (0.02 wt. % Pd / 0.06 wt. % Ag / 0.3 wt. % K / 0.3 wt. % F)					
<sup>d</sup>	Catalyst D (0.025 wt. % Pd / 0.01 wt. % Ag / 0.1 wt. % K / 0.05 wt. % F)					
<sup>e</sup>	Catalyst E (0.025 wt. % Pd / 0.04 wt. % Ag / 0.1 wt. % K / 0.05 wt. % F)					
<sup>f</sup>	Catalyst F (0.02 wt. % Pd / 0.005 wt. % Ag / 0.5 wt. % K / 0.5 wt. % F)					
<sup>g</sup>	Catalyst G (0.02 wt. % Pd / 0.06 wt. % Ag / 0.5 wt. % K / 0.5 wt. % F)					
<sup>h</sup>	C <sub>2</sub> denotes ethane					
<sup>i</sup>	C <sub>4</sub> denotes hydrocarbons containing 4 carbon atoms					
<sup>j</sup>	Heavies denotes hydrocarbons containing 6 or more carbon atoms					
<sup>k</sup>	ND denotes Not Determined					

Test data in Table I clearly show that the Invention Catalysts performed better than the Control Catalysts in several key areas of hydrogenation such as T1 and selectivity to various hydrocarbon compounds. The data demonstrate that the Invention Catalysts using low amounts of silver performed better than the Control Catalysts which used higher amounts of silver.

In the absence of COS, Invention Catalyst A exhibited a lower T1 and a similar ΔT when compared to Control Catalysts B and C. Also, in the

absence of COS, Invention Catalyst A demonstrated a decrease in heavies selectivity when compared to Control Catalysts B and C. In the presence of COS, Invention Catalyst A exhibited a greater  $\Delta T$  and a similar T1 when compared to Control Catalysts B and C. Furthermore, in the presence of COS, the C<sub>4</sub> and heavies selectivities for Invention Catalyst A were better than Control Catalysts B and C. The data demonstrate that the Invention Catalysts using low amounts of silver performed better than the Control Catalysts which used higher amounts of silver.

In addition, in the absence of COS, Invention Catalyst D exhibited a lower T1 compared to Control Catalyst E. In the presence of COS, Invention Catalyst D exhibited a lower T1 compared to Control Catalyst E as well as better ethane (C<sub>2</sub>) selectivity. Also, in the absence of COS, Invention Catalyst F exhibited a lower T1 compared to Control Catalyst G. Again, the data demonstrate that the Invention Catalysts using low amounts of silver performed better than the Control Catalysts which used higher amounts of silver.

The results shown in the above examples clearly demonstrate that the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those inherent therein.

Reasonable variations, modifications, and adaptations can be made within the scope of the disclosure and the appended claims without departing from the scope of this invention.

CLAIMS

1. A process comprising contacting a hydrocarbon-containing fluid, which comprises a highly unsaturated hydrocarbon, with a catalyst composition in the presence of hydrogen in a hydrogenation zone under a hydrogenation condition  
5 effective to hydrogenate said highly unsaturated hydrocarbon to a less unsaturated hydrocarbon wherein said catalyst composition comprises palladium, an inorganic support, and a catalyst component comprising silver and an alkali metal compound.
2. A process according to claim 1, wherein said highly unsaturated hydrocarbon is selected from the group consisting of alkynes, diolefins, and  
10 combinations thereof.
3. A process according to claim 2, wherein said alkynes are selected from the group consisting of acetylene, propyne, 1-butyne, 2-butyne, 1-pentyne, 2-pentyne, 3-methyl-1-butyne, 1-hexyne, 1-heptyne, 1-octyne, 1-nonyne, 1-decyne, and combinations thereof.
- 15 4. A process according to claim 2, wherein said diolefins contain in the range of from 3 carbon atoms per molecule to about 12 carbon atoms per molecule.
5. A process according to claim 4, wherein said diolefins are selected from the group consisting of propadiene, 1,2-butadiene, 1,3-butadiene, isoprene, 1,2-pentadiene, 1,3-pentadiene, 1,4-pentadiene, 1,2-hexadiene, 1,3-hexadiene,  
20 1,4-hexadiene, 1,5-hexadiene, 2-methyl-1,2-pentadiene, 2,3-dimethyl-1,3-butadiene, heptadienes, methylhexadienes, octadienes, methylheptadienes, dimethylhexadienes, ethylhexadienes, trimethylpentadienes, methyl-octadienes, dimethylheptadienes, ethyloctadienes, trimethylhexadienes, nonadienes, decadienes, undecadienes, dodecadienes, cyclopentadienes, cyclohexadienes, methylcyclopentadienes,  
25 cycloheptadienes, methylcyclohexadienes, dimethylcyclopentadienes, ethylcyclopentadienes, dicyclopentadiene (also known as tricyclo[5.2.1]<sup>2,6</sup>deca-3,8-diene), and combinations thereof.
6. A process according to claim 1, wherein said less unsaturated hydrocarbon is selected from the group consisting of ethylene, propylene, 1-butene,  
30 2-butene, isobutylene, 1-pentene, 2-pentene, methyl-1-butenes, methyl-2-butenes, 1-hexene, 2-hexene, 3-hexene, methyl-1-pentenenes, 2,3-dimethyl-1-butene, 1-heptene, 2-heptene, 3-heptene, methyl-1-hexenes, methyl-2-hexenes, methyl-3-hexenes,

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dimethylpentenes, ethylpentenes, octenes, methylheptenes, dimethylhexenes, ethylhexenes, nonenes, methyloctenes, dimethylheptenes, ethylheptenes, trimethylhexenes, cyclopentene, cyclohexene, methylcyclopentene, cycloheptene, methylcyclohexene, dimethylcyclopentenes, ethylcyclopentenes, cyclooctenes, methylcycloheptenes, dimethylcyclohexenes, ethylcyclohexenes, trimethylcyclohexenes, methylcyclooctenes, dimethylcyclooctenes, ethylcyclooctenes, and combinations thereof.

7. A process according to claim 1, wherein said process further comprises the presence of a sulfur impurity.

8. A process according to claim 7, wherein said sulfur impurity is a sulfur compound selected from the group consisting of hydrogen sulfide, carbonyl sulfide (COS), carbon disulfide (CS<sub>2</sub>), mercaptans (RSH), organic sulfides (R-S-R), organic disulfides (R-S-S-R), thiophene, substituted thiophenes, organic trisulfides, organic tetrasulfides, and combinations thereof, wherein said R can be an alkyl or cycloalkyl or aryl group containing 1 carbon atom to 10 carbon atoms.

9. A process according to claim 8, wherein said sulfur compound is present in said hydrocarbon-containing fluid at a concentration in the range of from about 0.5 part sulfur per billion parts hydrocarbon-containing fluid by volume to about 1000 parts sulfur per million parts hydrocarbon-containing fluid by volume.

10. A process according to claim 1, wherein said hydrocarbon-containing fluid further comprises a monoolefin.

11. A process according to claim 10, wherein said monoolefin is selected from the group consisting of ethylene, propylene, 1-butene, 2-butene, isobutylene, 1-pentene, 2-pentene, methyl-1-butenes, methyl-2-butenes, 1-hexene, 2-hexene, 3-hexene, methyl-1-pentenenes, 2,3-dimethyl-1-butene, 1-heptene, 2-heptene, 3-heptene, methyl-1-hexenes, methyl-2-hexenes, methyl-3-hexenes, dimethylpentenes, ethylpentenes, octenes, methylheptenes, dimethylhexenes, ethylhexenes, nonenes, methyloctenes, dimethylheptenes, ethylheptenes, trimethylhexenes, cyclopentene, cyclohexene, methylcyclopentene, cycloheptene, methylcyclohexene, dimethylcyclopentenes, ethylcyclopentenes, cyclooctenes, methylcycloheptenes, dimethylcyclohexenes, ethylcyclohexenes, trimethylcyclohexenes, methylcyclooctenes, dimethylcyclooctenes, ethylcyclooctenes, and combinations

thereof.

12. A process according to claim 11, wherein said hydrocarbon-containing fluid further comprises a saturated hydrocarbon selected from the group consisting of methane, ethane, propane, butane, methylpropane, methylbutane,  
5 dimethylbutane, pentanes, hexanes, and combinations thereof.

13. A process according to claim 1, wherein said hydrogenation condition comprises a temperature in the range of from about 10°C to about 300°C.

14. A process according to claim 13, wherein said hydrogenation condition further comprises a pressure in the range of from about 136 kPa to about  
10 13.88 MPa (about 5 pounds per square inch gauge (psig) to about 2000 psig).

15. A process according to claim 14, wherein said hydrogenation condition further comprises a charge rate of said hydrocarbon-containing fluid to said hydrogenation zone such as to provide a gas hourly space velocity in the range of from about 1 to about 50,000 liters of hydrocarbon-containing fluid per liter of  
15 catalyst per hour (liter/liter/hour).

16. A process according to claim 1, wherein said alkali metal compound is selected from the group consisting of alkali metal halides, alkali metal hydroxides, alkali metal carbonates, alkali metal bicarbonates, alkali metal nitrates, alkali metal carboxylates, and combinations thereof.

- 20 17. A process according to claim 16, wherein said alkali metal compound is an alkali metal halide which is an alkali metal iodide or an alkali metal fluoride.

18. A process according to claim 17, wherein the alkali metal of said alkali metal compound is selected from the group consisting of potassium, rubidium, cesium, and combinations thereof.

- 25 19. A process according to claim 18, wherein said alkali metal compound is potassium fluoride.

20. A process according to claim 1, wherein said catalyst composition has an amount of said palladium in the range of from about 0.0001 to about 3 weight percent palladium (as palladium metal) based on the total weight of said catalyst  
30 composition.

21. A process according to claim 1, wherein said catalyst composition has an amount of said silver in the range of from about 0.0003 to about 0.06 weight

percent silver (as silver metal) based on the total weight of said catalyst composition and said catalyst composition has an amount of alkali metal in the range of from about 0.001 to about 10 weight percent alkali metal based on the total weight of said catalyst composition

5 22. A process according to claim 21, wherein said catalyst composition has an amount of said silver in the range of from about 0.0005 to about 0.02 weight percent silver (as silver metal) based on the total weight of the said catalyst composition.

23. A process according to claim 21, wherein said catalyst composition  
10 has an amount of alkali metal in the range of from about 0.005 to about 5 weight percent alkali metal based on the total weight of said catalyst composition.

24. A process according to claim 1, wherein said catalyst composition further comprises a halide.

25. A process according to claim 24, wherein said catalyst composition  
15 has an amount of said halide in the range of from about 0.001 to about 10 weight percent said halide based on the total weight of said catalyst composition.

26. A process according to claim 25, wherein said halide is of a non-alkali metal halide.

27. A process according to claim 26, wherein said halide is a fluoride.

20 28. A process according to claim 27, wherein said non-alkali metal halide is selected from the group consisting of HF,  $\text{NH}_4\text{F}$ ,  $\text{NH}_4\text{HF}_2$ , and combinations thereof.

29. A process according to claim 1, wherein said inorganic support is selected from the group consisting of alumina, silica, zirconia, titania, an  
25 aluminosilicate, a spinel, zinc titanate, and combinations thereof.

30. A process according to claim 29, wherein said inorganic support is alumina and wherein said alumina is selected from the group consisting of alpha alumina, beta alumina, delta alumina, eta alumina, gamma alumina, theta alumina, and combinations thereof.

30 31. A catalyst composition comprising palladium, an inorganic support, and a catalyst component comprising silver and an alkali metal compound.

32. A catalyst composition according to claim 31, wherein said alkali

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metal compound is selected from the group consisting of alkali metal halides, alkali metal hydroxides, alkali metal carbonates, alkali metal bicarbonates, alkali metal nitrates, alkali metal carboxylates, and combinations thereof.

33. A catalyst composition according to claim 32, wherein said alkali  
5 metal compound is an alkali metal halide which is an alkali metal iodide or an alkali metal fluoride.

34. A catalyst composition according to claim 33, wherein the alkali metal of said alkali metal compound is selected from the group consisting of potassium, rubidium, cesium, and combinations thereof.

10 35. A catalyst composition according to claim 34, wherein said alkali metal compound is potassium fluoride.

36. A catalyst composition according to claim 31, wherein said catalyst composition has an amount of said palladium in the range of from about 0.0001 to about 3 weight percent palladium (as palladium metal) based on the total weight of  
15 the said catalyst composition.

37. A catalyst composition according to claim 31, wherein said catalyst composition has an amount of said silver in the range of from about 0.0003 to about 0.06 weight percent silver (as silver metal) based on the total weight of said catalyst composition and said catalyst composition has an amount of alkali metal in the  
20 range of from about 0.001 to about 10 weight percent alkali metal based on the total weight of said catalyst composition.

38. A catalyst composition according to claim 37, wherein said catalyst composition has an amount of said silver in the range of from about 0.0005 to about 0.02 weight percent silver (as silver metal) based on the total weight of said catalyst  
25 composition.

39. A catalyst composition according to claim 37, wherein said catalyst composition has an amount of alkali metal in the range of from about 0.005 to about 5 weight percent alkali metal based on the total weight of said catalyst composition.

30 40. A catalyst composition according to claim 31, wherein said catalyst composition further comprises a halide.

41. A catalyst composition according to claim 40, wherein said catalyst



composition has an amount of said halide in the range of from about 0.001 to about 10 weight percent said halide based on the total weight of said catalyst composition.

42. A catalyst composition according to claim 41, wherein said halide is of a non-alkali metal halide.

5 43. A catalyst composition according to claim 42, wherein said halide is a fluoride.

44. A catalyst composition according to claim 43, wherein said non-alkali metal halide is selected from the group consisting of HF,  $\text{NH}_4\text{F}$ ,  $\text{NH}_4\text{HF}_2$ , and combinations thereof.

10 45. A catalyst composition according to claim 31, wherein said inorganic support is selected from the group consisting of alumina, silica, zirconia, titania, an aluminosilicate, a spinel, zinc titanate, and combinations thereof.

46. A catalyst composition according to claim 45, wherein said inorganic support is alumina and wherein said alumina is selected from the group consisting  
15 of alpha alumina, beta alumina, delta alumina, eta alumina, gamma alumina, theta alumina, and combinations thereof.

47. A process of making a catalyst composition comprising incorporating an inorganic support with palladium and a catalyst component comprising silver and an alkali metal compound.

20 48. A process according to claim 47, wherein said palladium is present in a palladium compound selected from the group consisting of palladium bromide, palladium chloride, palladium iodide, palladium nitrate, palladium nitrate hydrate, tetraamine palladium nitrate, palladium oxide, palladium oxide hydrate, palladium sulfate, and combinations thereof.

25 49. A process according to claim 47, wherein said silver is present in a silver compound selected from the group consisting of silver nitrate, silver acetate, silver cyanide and combinations thereof.

50. A process according to claim 47, wherein said alkali metal compound is selected from the group consisting of alkali metal halides, alkali metal  
30 hydroxides, alkali metal carbonates, alkali metal bicarbonates, alkali metal nitrates, alkali metal carboxylates, and combinations thereof.

51. A process according to claim 48, wherein said palladium compound

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is palladium chloride and wherein hydrochloric acid has been added to said palladium chloride to form a  $\text{PdCl}_4^{-2}$  complex.

52. A process according to claim 50, wherein said alkali metal compound is an alkali metal halide which is an alkali metal iodide or an alkali metal fluoride.

5 53. A process according to claim 52, wherein the alkali metal of said alkali metal compound is selected from the group consisting of potassium, rubidium, cesium, and combinations thereof.

54. A process according to claim 53, wherein said alkali metal compound is potassium fluoride.

10 55. A process according to claim 48, wherein said palladium compound is present in a palladium-containing solution wherein the concentration of said palladium compound in said palladium-containing solution provides a catalyst composition having an amount of said palladium in the range of from about 0.0001 to about 3 weight percent palladium (as palladium metal) based on the total weight  
15 of said catalyst composition.

56. A process according to claim 49, wherein said silver compound is present in a silver-containing solution wherein the concentration of said silver compound in said silver-containing solution provides a catalyst composition having an amount of said silver in the range of from about 0.0003 to about 0.06 weight  
20 percent silver (as silver metal) based on the total weight of said catalyst composition.

57. A process according to claim 50, wherein said alkali metal compound is present in an alkali metal compound-containing solution wherein the concentration of said alkali metal compound in said alkali metal compound-  
25 containing solution provides a catalyst composition having an amount of alkali metal in the range of from about 0.001 to about 10 weight percent alkali metal based on the total weight of said catalyst composition.

58. A process according to claim 50, wherein said alkali metal compound is an alkali metal fluoride and further wherein said alkali metal fluoride is present in  
30 an alkali metal fluoride-containing solution wherein the concentration of said alkali metal fluoride in said alkali metal fluoride-containing solution provides a catalyst composition having an amount of alkali metal in the range of from about 0.001 to

about 10 weight percent alkali metal based on the total weight of said catalyst composition.

59. A process according to claim 47, wherein said process further comprises incorporating said inorganic support with a halide and further wherein  
5 said halide is present in a halide-containing solution wherein the concentration of said halide in said halide-containing solution provides a catalyst composition having an amount of said halide in the range of from about 0.001 to about 10 weight percent said halide based on the total weight of said catalyst composition.

60. A process according to claim 59, wherein said halide is of a non-  
10 alkali metal halide.

61. A process according to claim 60, wherein said halide is a fluoride.

62. A process according to claim 61, wherein said non-alkali metal halide is selected from the group consisting of HF,  $\text{NH}_4\text{F}$ ,  $\text{NH}_4\text{HF}_2$ , and combinations thereof.

15 63. A process according to claim 47, wherein said process of making a catalyst composition further comprises drying, under a composition drying condition, wherein said composition drying condition comprises:

a temperature in the range of from about 35°C to about 290°C,

20 a time period generally in the range of from about 0.1 hour to about 6 hours, and

a pressure in the range of from about atmospheric to about 689 kPa (about 100 pounds per square inch absolute).

64. A process according to claim 63, wherein said process of making a catalyst composition further comprises calcining, under a composition calcining  
25 condition, wherein said composition calcining condition comprises:

calcining in air or in a non-oxidizing gas atmosphere,

a temperature in the range of from about 200°C to about 900°C,

a time period in the range of from about 0.5 hour to about 40 hours,

and

30 a pressure in the range of from about 48.2 kPa to about 5.17 MPa (about 7 pounds per square inch absolute (psia) to about 750 psia).

65. A composition prepared by the process of any one of preceding

claims 47-64.

66. A process comprising contacting a hydrocarbon-containing fluid, which comprises a highly unsaturated hydrocarbon, with a catalyst composition in the presence of hydrogen in a hydrogenation zone under a hydrogenation condition effective to hydrogenate said highly unsaturated hydrocarbon to a less unsaturated hydrocarbon wherein said catalyst composition is prepared by the process according to any one of preceding claims 47-64.

67. A process according to claim 66, wherein said highly unsaturated hydrocarbon is selected from the group consisting of alkynes, diolefins, and combinations thereof.

68. A process according to claim 67, wherein said alkynes are selected from the group consisting of acetylene, propyne, 1-butyne, 2-butyne, 1-pentyne, 2-pentyne, 3-methyl-1-butyne, 1-hexyne, 1-heptyne, 1-octyne, 1-nonyne, 1-decyne, and combinations thereof.

69. A process according to claim 67, wherein said diolefins contain in the range of from 3 carbon atoms per molecule to about 12 carbon atoms per molecule.

70. A process according to claim 69, wherein said diolefins are selected from the group consisting of propadiene, 1,2-butadiene, 1,3-butadiene, isoprene, 1,2-pentadiene, 1,3-pentadiene, 1,4-pentadiene, 1,2-hexadiene, 1,3-hexadiene, 1,4-hexadiene, 1,5-hexadiene, 2-methyl-1,2-pentadiene, 2,3-dimethyl-1,3-butadiene, heptadienes, methylhexadienes, octadienes, methylheptadienes, dimethylhexadienes, ethylhexadienes, trimethylpentadienes, methyloctadienes, dimethylheptadienes, ethyloctadienes, trimethylhexadienes, nonadienes, decadienes, undecadienes, dodecadienes, cyclopentadienes, cyclohexadienes, methylcyclopentadienes, cycloheptadienes, methylcyclohexadienes, dimethylcyclopentadienes, ethylcyclopentadienes, dicyclopentadiene (also known as tricyclo[5.2.1]<sup>2,6</sup>deca-3,8-diene), and combinations thereof.

71. A process according to claim 66, wherein said less unsaturated hydrocarbon is selected from the group consisting of ethylene, propylene, 1-butene, 2-butene, isobutylene, 1-pentene, 2-pentene, methyl-1-butenes, methyl-2-butenes, 1-hexene, 2-hexene, 3-hexene, methyl-1-pentenenes, 2,3-dimethyl-1-butene, 1-heptene, 2-heptene, 3-heptene, methyl-1-hexenes, methyl-2-hexenes, methyl-3-hexenes,

dimethylpentenes, ethylpentenes, octenes, methylheptenes, dimethylhexenes, ethylhexenes, nonenes, methyloctenes, dimethylheptenes, ethylheptenes, trimethylhexenes, cyclopentene, cyclohexene, methylcyclopentene, cycloheptene, methylcyclohexene, dimethylcyclopentenes, ethylcyclopentenes, cyclooctenes, methylcycloheptenes, dimethylcyclohexenes, ethylcyclohexenes, trimethylcyclohexenes, methylcyclooctenes, dimethylcyclooctenes, ethylcyclooctenes, and combinations thereof.

72. A process according to claim 66, wherein said process further comprises the presence of a sulfur impurity.

73. A process according to claim 72, wherein said sulfur impurity is a sulfur compound selected from the group consisting of hydrogen sulfide, carbonyl sulfide (COS), carbon disulfide (CS<sub>2</sub>), mercaptans (RSH), organic sulfides (R-S-R), organic disulfides (R-S-S-R), thiophene, substituted thiophenes, organic trisulfides, organic tetrasulfides, and combinations thereof, wherein said R can be an alkyl or cycloalkyl or aryl group containing 1 carbon atom to 10 carbon atoms.

74. A process according to claim 73, wherein said sulfur compound is present in said hydrocarbon-containing fluid at a concentration in the range of from about 0.5 part sulfur per billion parts hydrocarbon-containing fluid by volume to about 1000 parts sulfur per million parts hydrocarbon-containing fluid by volume.

75. A process according to claim 66, wherein said hydrocarbon-containing fluid further comprises a monoolefin.

76. A process according to claim 75, wherein said monoolefin is selected from the group consisting of ethylene, propylene, 1-butene, 2-butene, isobutylene, 1-pentene, 2-pentene, methyl-1-butenes, methyl-2-butenes, 1-hexene, 2-hexene, 3-hexene, methyl-1-pentenenes, 2,3-dimethyl-1-butene, 1-heptene, 2-heptene, 3-heptene, methyl-1-hexenes, methyl-2-hexenes, methyl-3-hexenes, dimethylpentenes, ethylpentenes, octenes, methylheptenes, dimethylhexenes, ethylhexenes, nonenes, methyloctenes, dimethylheptenes, ethylheptenes, trimethylhexenes, cyclopentene, cyclohexene, methylcyclopentene, cycloheptene, methylcyclohexene, dimethylcyclopentenes, ethylcyclopentenes, cyclooctenes, methylcycloheptenes, dimethylcyclohexenes, ethylcyclohexenes, trimethylcyclohexenes, methylcyclooctenes, dimethylcyclooctenes, ethylcyclooctenes, and combinations

thereof.

77. A process according to claim 76, wherein said hydrocarbon-containing fluid further comprises a saturated hydrocarbon selected from the group consisting of methane, ethane, propane, butane, methylpropane, methylbutane,  
5 dimethylbutane, pentanes, hexanes, and combinations thereof.

78. A process according to claim 66, wherein said hydrogenation condition comprises a temperature in the range of from about 10°C to about 300°C.

79. A process according to claim 78, wherein said hydrogenation condition further comprises a pressure in the range of from about 136 kPa to about  
10 13.88 MPa (about 5 pounds per square inch gauge (psig) to about 2000 psig) and a charge rate of said hydrocarbon-containing fluid to said hydrogenation zone such as to provide a gas hourly space velocity in the range of from about 1 to about 50,000 liters of hydrocarbon-containing fluid per liter of catalyst per hour (liter/liter/hour).

## INTERNATIONAL SEARCH REPORT

 International application No.  
PCT/US00/42068
**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : B01J 23/58, 23/66; C07C 7/167, 5/05, 5/08

US CL : 585/259, 260, 261, 271; 502/327, 333, 348

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/259, 260, 261, 271; 502/327, 333, 348

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST

Search terms: hydrogenation, highly unsaturated alkyne, alkkadiene, selective hydrogenation

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,698,752 A (BROWN et al) 16 December 1997, abstract, col. 1, lines 40-60, col. 2, lines 1-68; col. 6, lines 35-50, claims.	1-79
X	US 5,866,735 A (CHEUNG et al) 02 February 1999, abstract, col. 2, lines 45-55, col. 4, line 60 - col. 5, line 60, example 1, table 1, claims.	1-79
X	US 5,648,576 A (NGUYEN THAN et al) 15 July 1997, abstract, col. 2, lines 20-36, 60-68, col. 3, lines 1-68, claims.	1- 79



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

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23 APRIL 2001

Date of mailing of the international search report

08 MAY 2001

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